

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

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NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year) 13.07.2001

Applicant's or agent's file reference
ICIX/P22915PC

IMPORTANT NOTIFICATION

International application No.
PCT/GB00/01861

International filing date (day/month/year)
15/05/2000

Priority date (day/month/year)
18/05/1999

Applicant
INEOS FLUOR HOLDINGS LIMITED et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference ICIX/P22915PC	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB00/01861	International filing date (day/month/year) 15/05/2000	Priority date (day/month/year) 18/05/1999
International Patent Classification (IPC) or national classification and IPC C07C17/087		
Applicant INEOS FLUOR HOLDINGS LIMITED et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☒ Certain defects in the international application
 - VIII ☐ Certain observations on the international application

Date of submission of the demand 29/11/2000	Date of completion of this report 13.07.2001
Name and mailing address of the international preliminary examining authority: <div style="margin-left: 20px;">  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465 </div>	Authorized officer Sen, A Telephone No. +49 89 2399 8328 <div style="text-align: right;">  </div>

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB00/01861

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-3,7,9 as originally filed

4-6,8 as received on 23/05/2001 with letter of 22/05/2001

Claims, No.:

1-8 as received on 23/05/2001 with letter of 22/05/2001

Drawings, sheets:

1/4-4/4 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

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EXAMINATION REPORT**

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- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-8
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-8
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-8
	No:	Claims	

- 2. Citations and explanations**
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

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EXAMINATION REPORT - SEPARATE SHEET**

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SECTION V:

D1: EP-A-0 509 885
D2: WO 99 26907 A
D3: WO 99 51555 A

The amendments made do not introduce subject-matter that was not present in the application as originally filed. In particular, the new claim 5 finds basis on page 4, lines 11 to 14. Renumbered claims 6 and 7 are dependent on the new claim 5. It is however clear from the text on page 4, lines 14 to 16 that additional hexafluoropropene (HFP) can be charged to the reactor or to the liquid phase separator.

The subject-matter of the present application directed to a process for the production of 1,1,1,2,3,3,3-heptafluoropropane (HFC 227ea) meets the requirements of Article 33(2) PCT since the prior art documents cited in the International Search Report do not describe the same preparation of HFC 227ea / separation of HFC 227ea from HF. D1 describes the separation of HF from 1,1,1-trifluoro-2-chloroethane. D2 describes the reaction between HFP and HF for the preparation of HFC 227ea. In particular, with regard to the separation of HFC 227ea from HF the document describes that the fluorine containing organic compound substantially free of hydrogen fluoride and the haloalkene/hydrogen fluoride azeotrope can be separated by charging the reaction product and the haloalkene to a distillation column and distilling the resulting mixture [D2: claim 1]. D3 describes a process for the separation of a mixture comprising HF and $\text{CF}_3\text{CClFCF}_3$.

The problem to be solved is the provision of an improved process for the production of HFC 227ea by improving the separation of HFC 227ea from HF. As discussed in the application HFC 227ea and HF as well as the ternary mixture of HF, HFC 227ea and HFP are known to form azeotropes and azeotrope-like mixtures which are difficult to separate by methods such as distillation.

This problem is solved according to the present application by charging the reaction mixture from the reaction of HFP and HF into a liquid phase separator so that two different phases can be separated. As shown in Example 1, the reaction mixture comprising HFC 227ea, HFP and HF spontaneously separates into two liquid phases, an organic phase and a HF phase in the liquid-phase separator [see also Table on

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EXAMINATION REPORT - SEPARATE SHEET**

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page 9]. Such approach is not suggested in the cited prior art which deals or with different mixtures of compounds or with different solutions, e.g. distillation.

The requirements of inventive step under Art. 33(3) PCT appear accordingly to be met.

SECTION VII:

1. To meet the requirements of Rule 5.1(a)(ii) PCT, the documents D1 and D3 should be briefly identified in the description.
2. Claim 1 needs amendment with regard to the definition of HFP. Thus the expression "hexafluoropropane" should be corrected to read "hexafluoropropene".

The reaction mixture charged to the liquid-phase separator in Step A may be the mixture arising directly from the reactor in which HFP is reacted with hydrogen fluoride (direct mixture). It is often preferred, however, that the mixture charged to the liquid-phase separator is essentially an HFC 227ea/hydrogen fluoride azeotrope, for example obtained from distillation of the direct mixture.

It will be appreciated that the use of an HFC 227ea/HF azeotrope, or azeotrope-like mixture, in the process according to the present invention will not facilitate separation of the organic phase from the hydrogen fluoride-rich phase such use increases the amount of HFC 227ea to be removed per pass and, accordingly, reduces the amount of material to be recycled.

We have found surprisingly that addition of HFP facilitates separation of the HFC 227ea/hydrogen fluoride azeotrope into its components. The HFP may be introduced into the process according to the present invention at one or more appropriate points. For example, it may be charged to the reactor and/or to the liquid-phase separator in Step A and/or to the distillation column in Step C. Preferably the HFP is added to the liquid phase separator, either directly or mixed with the reaction mixture.

The reaction of HFP with hydrogen fluoride ~~in the process according to the first aspect of the present invention~~ may be carried out in the liquid phase or in the vapour phase.

To facilitate the separation in Step A of the process ~~according to the first aspect of the present invention~~, Step A is preferably carried out at below ambient temperature, typically at below 30°C.

To facilitate the separation in Step A of the process ~~according to the first aspect of the present invention~~, Step A is preferably carried out at supra-atmospheric pressure, typically 1-20 bars and preferably about 10 bars.

~~In a first embodiment of the process according to the first aspect of the present invention,~~ The product of the reaction of HFP with hydrogen fluoride ^{may be} distilled to recover a portion of the hydrogen fluoride therefrom before the mixture comprising HFC 227ea/hydrogen fluoride azeotrope or azeotrope-like mixture thereof, HFP/hydrogen fluoride azeotrope or azeotrope-like mixture thereof, and hydrogen fluoride is charged to the liquid phase separator in Step A.

The portion of hydrogen fluoride recovered by distillation in a recovery step prior to Step A, where such a recovery step is carried out, is preferably recycled to the reactor vessel.

5 ~~In a second embodiment of the process according to the first aspect of the present invention,~~ ^{Alternatively,} the product of the reaction of HFP with hydrogen fluoride ^{may be} charged directly to the liquid-phase separator in Step A.

Where HFC 227ea is prepared by reacting HFP with hydrogen fluoride in the ~~process according to the first aspect of the present invention in the~~ liquid phase in the presence of a catalyst, eg TaF₅, NbF₅, or SbF₅, it is suitably carried out at a temperature in 10 the range 20 to 200°C, preferably 40 to 120°C and especially 50 to 100°C. Suitably the reaction is carried out at superatmospheric pressure such that the reactants are in the liquid phase for sufficient time to react to produce HFC 227ea. Preferably the pressure is at least 5 bar and more preferably the pressure is 10 to 50 bar.

^A
15 ~~The residence time in the reactor in the process according to the first aspect of the present invention is~~ sufficient to permit conversion of HFP feedstock into HFC 227ea. ^{is required} The required residence time will be dependent on *inter alia* the degree of conversion required, the reactant ratio and the reaction conditions.

Where a low conversion rate of HFP into HFC 227ea is desired it is preferable that the feedstocks be recycled to increase the yield of HFC 227ea from the starting 20 material. However, we do not exclude the possibility that recycling is employed where high single pass conversions are required.

~~In the process according to the present invention~~ The molar ratio of hydrogen fluoride (HF) to HFP fed to the reactor is suitably at least 1:1 and preferably between 1.2 and 10:1. It will be appreciated that where a molar ratio of HF to HFP of 0.1 up to 1:1 is 25 employed the conversion ratio and/or the yield will be lower.

~~In the process according to the present invention~~ The molar ratio of HFP to the catalyst is suitably not more than 100:1 and is preferably between 1:1 and 50:1.

The levels of HF, HFP and catalyst in the process according to the present invention are suitably selected such that the catalyst and reactants are at least largely 30 dissolved in the liquid phase under the reaction conditions employed.

The process according to the present invention may be operated in batch or continuous mode as desired. Semi-batch operation may also be employed in which one

or more feedstocks are fed continuously to the process and one or more other feedstocks are fed to the process in batch-wise fashion.

Alternatively, ^{reaction of HFP and HF} ~~the process according to the present invention~~ may be carried out in the vapour phase. Suitable conditions and catalysts for use in carrying out the ^{reaction} ~~process~~ ^{of HFP and HF} ~~according to the present invention~~ in the vapour phase are more fully described in DE 2712732 and GB 902590 mentioned hereinbefore.

The present invention will be further illustrated by reference to the accompanying drawings which illustrate, by way of example only, schematic representations of plants for carrying out the process according to the present invention.

10 In the drawings:

Figure 1 is a schematic representation of a plant wherein HFP is fed to the liquid-phase separator;

Figure 2 is a schematic representation of a plant wherein HFP is fed to the reactor;

15 Figure 3 is a schematic representation of a plant wherein the product of the reaction is fed directly to the liquid-phase separator; and

Figure 4 is a ternary diagram illustrating HFC 227ea, HFP and HF separation.

In Figures 1 and 2, feed pipe (1) leads to a reactor (2), which optionally contains a fluorination catalyst. Product pipe (3) from the reactor (2) is in fluid-flow communication with a first distillation column (4), which is for example a single stage
20 flash vessel. Distillation column (4) is typically operated at a pressure of 12 bars with a bottoms temperature of 100°C and a tops temperature of around 50°C. Bottoms pipe (5) from distillation column (4) is in fluid-flow communication with feed-pipe (1). Tops line (6) from distillation column (4) is in fluid-flow communication with a liquid-phase separator (7). Tops line (8) from the liquid-phase separator (7) is in fluid-flow
25 communication with feed-pipe (1). Bottoms line (9) from the liquid-phase separator (7) is in fluid-flow communication with a second distillation column (10), which is for example a packed column. Distillation column (10) is typically operated at a pressure of around 12 bars with a tops temperature of 37°C and a bottoms temperature of around 60°C. Distillation column (10) is provided with an exit pipe for product (11) and a tops
30 pipe (12).

In Figure 1, tops pipe (12) from distillation column (10) is in fluid flow communication with tops line (6) which is provided with a feed-pipe (13).

unconverted HFP, often in the form of a ternary azeotrope, travels through product pipe (14) to the liquid-phase separator (7). HFP is fed via feed line (13) and product pipe (14) to liquid-phase separator (7). The liquid-phase separator (7) is typically operated at 0-20°C to afford better separation. In the liquid-phase separator (7), an HF-rich phase separates from the organics-rich phase. The HF-rich phase is returned via tops-line (8) to feed-pipe (1). The organics-rich phase flows via bottoms line (9) to distillation column (10). A stream comprising HFP and essentially all the hydrogen fluoride content of the stream entering distillation column (10) via line (9) is removed from the top of distillation column (10) via line (12) and returned to the liquid phase separator (7) via line (14). The product stream HFC 227ea is removed from the bottom of column (10) via exit pipe (11).

In the ternary diagram in Figure 4, compositions in the area of the figure designated A phase-separate, namely compositions comprising 0.4-0.6 mole % HF, greater than 0.4 mole % HFP and less than 0.6 mole % HFC 227ea. *frachon*

The present invention is further illustrated by reference to the following Examples.

Examples 1-4

These examples 1-4 illustrate the liquid-phase separation of HFP 227ea from HF and the enhanced separation thereof in the presence of HFP.

In the Examples, HFC 227ea and HFP, where used, were added to HF in a 500 ml whitey bomb cooled in liquid nitrogen. The whitey bomb was provided with a double-dip arrangement such that the dip-pipes would sample from the middle of each phase. The mixture was allowed to warm to room temperature, agitated, allowed to stand for 2 hours and then analysed.

The HF phase was analysed for organics by transferring a portion of the HF phase (10g) to a smaller whitey bomb containing water. It was allowed to stand for 15 minutes then the headspace was analysed by G.C.

The organics phase was analysed for HF by bubbling a portion of the organics phase through water scrubbers containing fresh de-ionised water and ice. The water was then analysed for fluoride.

The results are shown in the Table from which it can be seen that (a) a mixture of HFC 227ea and HF phase-separates such that an organic layer and an HF-rich layer are formed (Example 1) and (b) addition of HFP to the HFC 227ea/HF mixture reduces the

Claims

- 1,1,1,2,3,3,3-heptafluoropropane*
1. A process for the production of (HFC 227ea) by the reaction of (HFP) with hydrogen fluoride characterised by the Steps of *hexafluoropropane*
- 5 A. charging the reaction mixture from the reaction of HFP with hydrogen fluoride to a liquid-phase separator and allowing an organic phase and a hydrogen fluoride-rich phase to separate under gravity ;
- B. recycling the hydrogen fluoride-rich phase separated in Step A to the reactor in which the reaction is carried out;
- C. charging the organic-rich phase separated in Step A to a distillation column;
- 10 D. recovering the HFC 227ea and an hydrogen fluoride-rich mixture separately from the distillation column in Step (C); and
- E. recycling the hydrogen fluoride-rich mixture recovered from Step D to the reactor.
- 15 2. A process as claimed in Claim 1 wherein the reaction mixture charged to the liquid-phase separator in Step (A) comprises an HFC 227ea/HF azeotrope, or azeotrope-like mixture.
3. A process as claimed in Claim 1 wherein in Step A the organic phase and the hydrogen fluoride-rich phase are allowed to separate under gravity at below
- 20 ambient temperature.
4. A process as claimed in Claim 1 wherein in Step A the organic phase and the hydrogen fluoride-rich phase are allowed to separate under gravity at
- supra-atmospheric pressure
- 6 A process as claimed in Claim 5, *wherein the additional* further characterised in that the HFP is charged
- 25 to the liquid-phase separator.
78. A process as claimed in Claim 5, *wherein the additional* further characterised in that the HFP is charged
- to the reactor.
8. A process as claimed in any one of the preceding claims wherein the mixture to be separated in the liquid-phase separator in Step (A) comprises a mole ratio of
- 30 HF:HFC 227ea of between 3:7 and 6:4.
5. A process according to any one of the preceding claims in which HFP in addition to that present in the reaction mixture from the reaction of HFP with hydrogen fluoride is introduced into the process.

Claims

- 1,1,1,2,3,3,3-heptafluoropropane*
1. A process for the production of (HFC 227ea) by the reaction of (HFP) with hydrogen fluoride characterised by the Steps of
- hexafluoropropane
hexafluoropropene*
- 5 A. charging the reaction mixture from the reaction of HFP with hydrogen fluoride to a liquid-phase separator and allowing an organic phase and a hydrogen fluoride-rich phase to separate under gravity ;
- B. recycling the hydrogen fluoride-rich phase separated in Step A to the reactor in which the reaction is carried out;
- 10 C. charging the organic-rich phase separated in Step A to a distillation column;
- D. recovering the HFC 227ea and an hydrogen fluoride-rich mixture separately from the distillation column in Step (C); and
- E. recycling the hydrogen fluoride-rich mixture recovered from Step D to the reactor.
- 15 2. A process as claimed in Claim 1 wherein the reaction mixture charged to the liquid-phase separator in Step (A) comprises an HFC 227ea/HF azeotrope, or azeotrope-like mixture.
3. A process as claimed in Claim 1 wherein in Step A the organic phase and the hydrogen fluoride-rich phase are allowed to separate under gravity at below
- 20 ambient temperature.
4. A process as claimed in Claim 1 wherein in Step A the organic phase and the hydrogen fluoride-rich phase are allowed to separate under gravity at supra-atmospheric pressure
- 25 *6* A process as claimed in Claim 5, *wherein the additional* further characterised in that the HFP is charged to the liquid-phase separator.
- 7.8* A process as claimed in Claim 5, *wherein the additional* further characterised in that the HFP is charged to the reactor.
- 8.* A process as claimed in any one of the preceding claims wherein the mixture to be separated in the liquid-phase separator in Step (A) comprises a mole ratio of
- 30 HF:HFC 227ea of between 3:7 and 6:4.
5. A process according to any one of the preceding claims in which HFP in addition to that present in the reaction mixture from the reaction of HFP with hydrogen fluoride is introduced into the process.